

Texture Changes During the Quartz α - β Phase Transition Studied by Neutron Diffraction

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H.-R. Wenk, S. Grigull, J. Pehl (University of California at Berkeley), D.J. Williams (LANSCE Division)

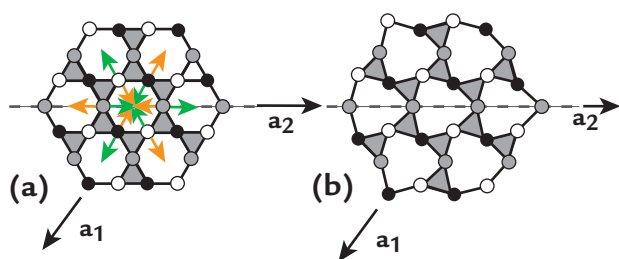


Fig. 1. A c-axis projection of the structure of quartz (a_1 and a_2 axes are indicated). Only silicon atoms are shown with patterns indicating different z-levels (the white, gray, and black circles). (a) Hexagonal β -phase quartz with potential distortions to trigonal α -phase quartz indicated by orange and green arrows. (b) Trigonal α -phase quartz representing one orientation variant produced by green-arrow distortions. The second variant, produced by orange-arrow distortions, would be related by a 180° rotation.

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hase transitions in polycrystals have a profound impact on physical properties of materials, in particular, on the anisotropy pattern, which is due to preferred orientation (or texture) of crystals. In general, textures are measured at room temperature, and high-temperature texture is implied by modeling. Time-of-flight neutron diffractometers, such as the High-Pressure-Preferred Orientation (HIPPO) instrument at LANSCE, have made *in situ* investigations of texture changes during phase transformations possible. We report here on texture changes for the displacive trigonal-hexagonal phase transition of quartz, which occurs at 573°C .

Exploring Texture Changes in Bulk Quartzite During α - β Phase Transitions

The α - β phase transition of quartz has long been of interest in crystallography.¹ Through slight atomic displacements, the high-temperature hexagonal structure (Fig. 1a) of quartz distorts to a trigonal structure upon cooling (Fig. 1b) without changing the orientation of the c-axis or the a-axes (a_1 and a_2). There are two orientation variants for trigonal quartz, related geometrically through

a 180° rotation about the c-axis and requiring only slight distortions of the crystal structure as indicated by the colored arrows in Fig. 1a. The β -phase quartz can be viewed as an average of two orientation variants of trigonal α -phase quartz. Upon cooling, crystals could assume either of these two orientations. Internal strains are critical for the variant selection, and this requires characterization of *bulk* materials where each grain is influenced by its surrounding neighbors. Many aspects of the α - β phase transformation in

quartz remained enigmatic because traditional investigations, such as x-ray diffraction and electron microscopy, relied on surface characterization. Thus neutron diffraction with minimal absorption offers unique opportunities. During the 2002 run cycle at LANSCE, we used the texture/temperature capabilities of HIPPO to explore the texture changes of bulk quartzite during the α - β phase transition and to resolve the question as to which trigonal orientation variant the material selects during subsequent cooling.

The unique features of HIPPO are high count rates, a large array of detectors, and a wide range of ancillary instruments for *in situ* low- and high-temperature and -pressure studies. With HIPPO, diffracted neutrons are detected by an array of 50 detector panels with 1,400 ^3He detector tubes located at different directions and diffraction angles. Only 30 detectors from the 40°, 90°, and 150° banks were used in our experiment because of limitations in resolution that decrease with diffraction angle (Fig. 2). It is possible to have 6 orientation angles about the vertical axis, resulting in $6 \times 30 = 180$ orientations (Fig. 3a). The size of each circle corresponds to the intensity for the 201 reflection and is proportional to the number of crystallites in that orientation. Fig. 3b is an averaged pole-density distribution for diffraction peak 201. HIPPO is equipped with a 300- to 2,000-K vacuum furnace for conducting *in situ* texture measurements as a function of temperature.

The sample used in our experiment was a naturally deformed fine-grained quartz mylonite with a simple texture that resembles a single crystal with a pronounced trigonal symmetry (i.e., a single c-axis maximum and three maxima for positive rhombs). The sample was mounted on a vanadium holder. Diffraction spectra were recorded for 500 s. The Rietveld analysis technique² could not be used because the diffraction spectra were contaminated by parasitic peaks originating from diffraction by the metal surface of the vacuum furnace. Instead, an automatic-intensity-extraction procedure for recording individual diffraction peaks was developed. The 180 corrected intensities at different pole-figure coordinates for 4 quartz diffraction peaks (100, 101, 201, and 112) were then used to calculate the orientation distribution.³ Diffraction peak 101 is a superposition of the 2 non-equivalent diffractions 101 and 011 with scattering

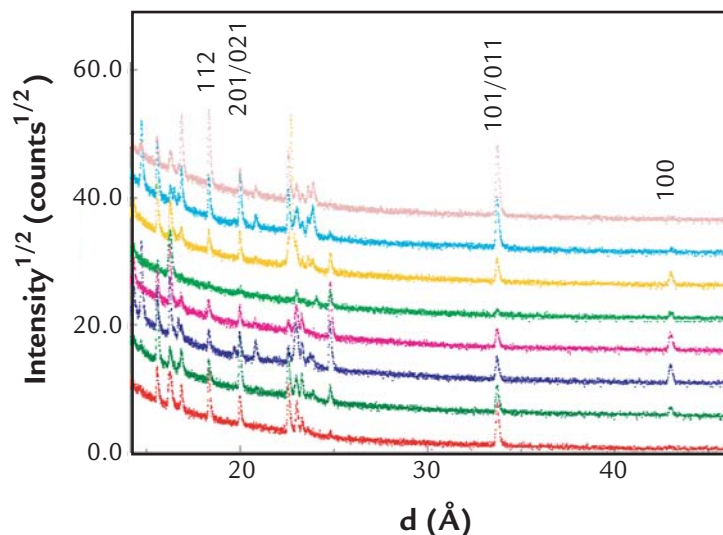


Fig. 2. Typical diffraction spectra for one rotation setting of the 150° bank. Diffraction peaks of quartz used in the texture analysis are indicated. Notice relative intensity variations between spectra that are due to texture. In addition to quartz peaks, there are numerous diffraction peaks from the furnace metal, which made the analysis difficult.

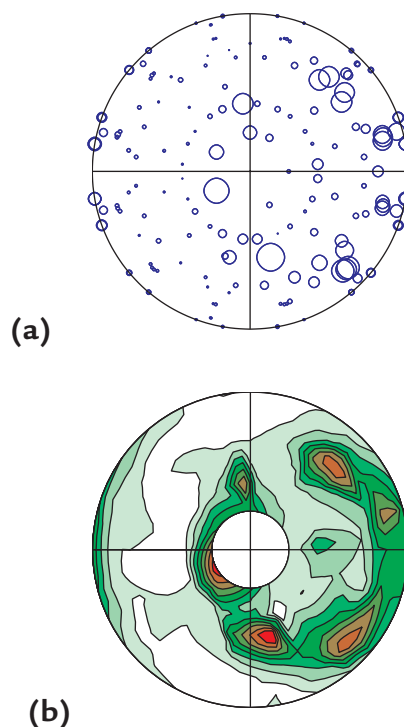


Fig. 3. Pole-figure coverage with 30 detectors on 150°, 90°, and 40° banks of HIPPO and 6 sample rotations. (a) The discrete circles represent detectors. The size of the circle is proportional to the intensity of the 201 crystal-plane reflection and thus the pole density in that direction. (b) Averaging of the discrete pole density produces a continuous coverage. Such incomplete pole figures were used for determining the orientation distribution.

contributions for neutrons of 70% and 30%, respectively. Peak 201 is a superposition of 201 and 021 with contributions of 20% and 80%, respectively. This intensity difference was used to resolve the trigonal texture symmetry.

From the orientation distribution, individual pole figures for 001 (c-axis), 100 (prism), 101, and 011 were recalculated (Fig. 4). Before the phase transition (Fig. 4a), we observed a strong texture with a single c-axis maximum — 100 poles are distributed on a great circle with 6 concentrations at 60° intervals, and 101 and 011 poles each show 3 slightly asymmetric concentrations related by a 120° rotation about the c-axis. Heating to 625°C did not change the 001 and 100 patterns, but texture intensities for rhombohedral (101 and 011) poles were distributed over a small circle with 6 concentrations consistent with hexagonal crystal symmetry (Fig. 4b). Upon cooling, the texture became trigonal again (Fig. 4c) and was identical with the starting texture — even for minor details. We obtained the same results upon repeating the heating-cooling cycle.

HIPPO Experiment Paves the Way for Studying Texture Changes During Heating

To our knowledge, this is the first *in situ* determination of texture changes during phase transformations by neutron diffraction. As such, the experiment opens a new field to investigate texture changes during heating. The 50-minute time period used to record data for one temperature interval allowed us to follow texture changes in real time. The results for quartzite clearly show that the aggregate retains its "shape memory" (the shape-memory effect refers to a phenomenon whereby a material, when mechanically deformed and then heated, returns

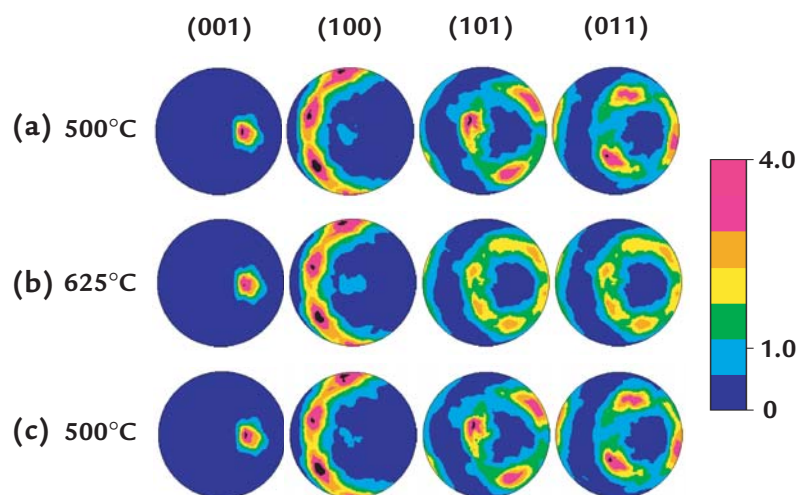


Fig. 4. Pole figures 001, 100, 101, and 011 for a metamorphic quartzite recalculated from the orientation distribution: (a) 500°C (before heating), (b) 625°C, (c) 500°C (after heating). Equal-area projection, linear-pole-density scale in multiples of a random distribution. The scale for the 001 pole figure needs to be multiplied by a factor of 5 relative to the others. The trigonal low-temperature texture becomes hexagonal upon heating and returns to exactly the same pattern upon cooling.

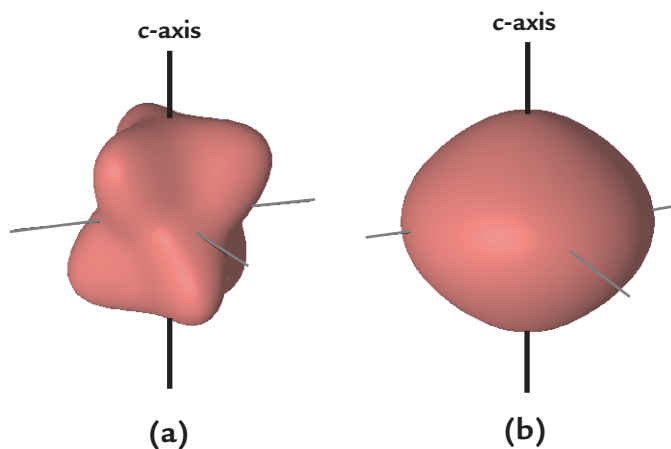


Fig. 5. Young's modulus for (a) trigonal α -phase quartz and (b) hexagonal β -phase quartz, illustrating the elastic anisotropy. The surfaces are normalized so that the maximum values are equal.

to its original shape). Quartzite thus emerges as a shape-memory system similar to those previously observed in some metals.⁴ When quartz becomes hexagonal upon heating, the orientation distribution also becomes hexagonal. Upon cooling, crystals could choose at random between the two possible trigonal orientation variants. Yet the memory

is retained, presumably by elastic strains imposed by neighboring grains, and crystals revert to their initial orientation. Contrary to β -phase quartz with a very weak elastic anisotropy⁵ and axial symmetry about the c-axis (Fig. 5a), α -phase quartz is elastically strongly anisotropic⁶ with a direction near 011 almost twice stiffer than one

near 101 (Fig. 5b). If the initial low-temperature microstructure is without internal strains, the phase transformation will thus impose large elastic stresses through compatibility requirements of neighboring grains. Those stresses will determine the orientation variant upon cooling. Because the preferred-orientation pattern depends on interaction between neighbors, polycrystalline bulk samples need to be characterized via neutron diffraction.

Conclusion

In this context, the issue of the stress field becomes relevant.⁷ Deformation experiments at low temperature documented texture changes owing to imposed stress with minimal macroscopic strain.⁸ If a stress is imposed during the phase transformation and the quartzite does not undergo significant plastic deformation at lower temperature, the active stress field will influence the variant selection, and the "trigonality" of the quartz texture could therefore be used as a piezometer of the ancient stress field in metamorphic rocks.⁹ (A piezometer is an instrument for measuring pressure, particularly high pressures.) The investigation of preferred orientation in many naturally deformed quartzites revealed that the orientation distribution of positive and negative rhombs is different. The texture has a trigonal symmetry with a great variety of natural quartz textures that form under different temperature, pressure, and strain conditions.¹⁰ Systematic transition experiments on different texture types and imposing stresses during the phase transitions can shed some light on the deformation behavior of this mineral, which is so important for plasticity in the Earth's crust.

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